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6. AUTHOR(S)

Alfred E. Asato
Robert S. H. Liu

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

University of Hawaii
Chemistry Department
2545 The Mall
Honolulu, Hawaii 96822

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13. ABSTRACT (Maximum 200 words)

A series of new symmetrical 1,3-disubstituted azulene derivatives were prepared for examination of their two-photon absorption and optical limiting properties. Several structurally modified azulenic polymethine dyes, previously identified as reverse saturable absorbers and optical limiters, were also prepared. Synthetic protocols were devised to covalently attach a number of azulenic NLO chromophores to polymer hosts. A completely unexpected nonequivalence was observed for one of the NMR signals for symmetrical polymethine dye 13c at low-temperature. The measurement of electronic properties (dipole moments, polarizabilities, and hyperpolarizabilities) of a series of fluorinated azulenic azobenzenes is being undertaken using electroabsorption (Stark) spectroscopy.

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Alfred E. Asato
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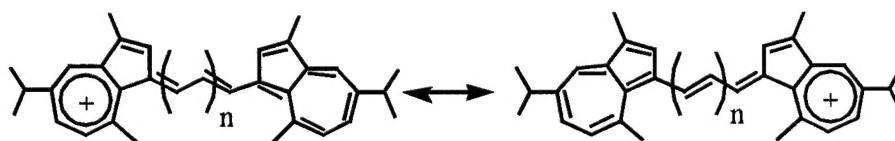
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I. Azulene-Containing Chromophores for Optical Limiting and Other NLO Applications

We have prepared a number of new compounds as part of our ongoing effort to synthesize azulene-containing nonlinear optical chromophores with enhanced excited state absorption cross sections for optical limiting and other important NLO applications. Several important chromophore structural features that gave rise to large optical nonlinearities were identified in previous collaborative projects with ARO scientists and other researchers.¹⁻⁸ In particular, azulenic polymethine cationic dyes, were singled out for further study.



1, $n = 0$; 2, $n = 1$; 3, $n = 2$; 4, $n = 3$

In contrast to conventional cyanine dyes that have heteroatoms as the π -electron donor, azulenic polymethine dyes feature the nonalternant 10π -electron aromatic hydrocarbon, azulene, as the π -electron donor, together with azulenyl cation as the π -electron acceptor.

The new thermally stable chromophores are optically transparent throughout the visible region for the longer chromophores and have a single relatively sharp, intense linear absorption maxima in the near IR. Absorption spectra for 1-4 are shown below (Fig. 1). Absorption maxima for the series of dyes are red-shifted by 0.16-0.19 eV per double bond. Azulenic dye 4 is essentially optically transparent below 500 nm.



Fig. 1. Absorption maxima for azulenic polymethine dyes 1-4 in CH_2Cl_2 . Absorbances are not to scale.

Third-order NLO susceptibilities $\chi^{(3)}$ and nonlinear refractive indices were measured for several members of this new class of NLO chromophore. The predominant mechanism for their NLO activity was reverse saturable absorption. Very weak fluorescence was observed for an azulenic trimethine salt.⁷

Symmetrical azulenic chromophores

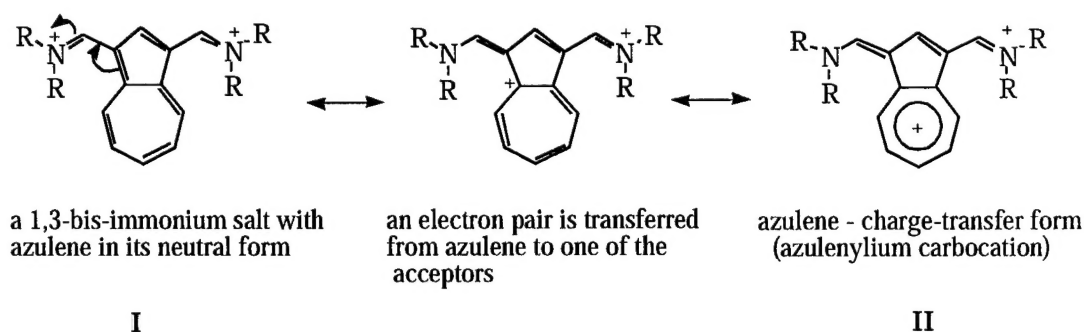
Although both first and second hyperpolarizabilities as well as other NLO properties for our compounds compare favorably to traditional heteroatom-containing donor-acceptor molecules, little is currently known of the NLO behavior of symmetrical azulene-containing quadrupolar compounds. Marder and Perry have already demonstrated that conjugated molecules with donor- π -donor and acceptor- π -acceptor structural motifs have large two-photon excited state cross sections.^{9,10} More recently Van Stryland and Hagan has reported on the 2PA activity of amine-substituted fluorene derivatives with various acceptor groups using their femtosecond pump/white light continuum probe "NLO spectrometer."¹¹

Toward the goal of elucidating 2PA and other excited state properties including optical limiting behavior in collaboration with future collaborators we have prepared and characterized a number of symmetrical and nonsymmetrical azulenic chromophores. A partial list is shown below (page 4).

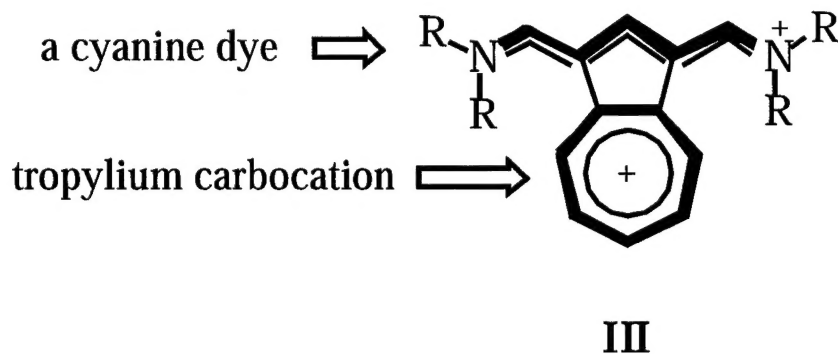
New 1,3-Disubstituted Azulene Chromophores for Third-Order Nonlinear Optical Applications. A Case of a Chromophore in a Chromophore?

The extent of electron transfer from the seven-member ring of azulene (the "pre-tropylium ion" end) to a π -electron acceptor group depends upon the position of attachment of the acceptor group on the ring. With the acceptor group attached to the C1-position of azulene, electron transfer is facilitated in the ground state by formation of a new resonance stabilized species, the azulenylum carbocation, a Hückel aromatic 6π -electron system (formally, a tropylium carbocation). This special stabilizing effect is absent when the acceptor is attached to the C2-position of the azulene ring.

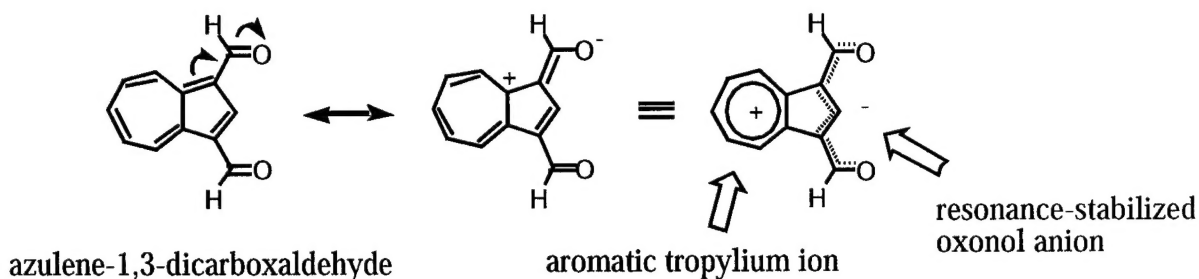
An interesting situation arises when two electron withdrawing substituents are attached to both the C1- and C3-positions as shown below. There is no resonance interaction between the two acceptors in the neutral ground state form. Furthermore, electron transfer involves only one acceptor, but not the other.



However, after electron transfer a new conjugation pathway is opened between the two acceptors! The electronic structure is that of a cyanine dye attached to a tropylium carbocation with one of the positive charges "localized" in the cyanine dye portion and the other positive charge "localized" in the resonance-stabilized tropylium ring system. Such a "composite" structure might conceivably arise by lengthening of the two five-member ring bonds connecting the two separate chromophores in either the neutral, I, or charge-separated form, II.



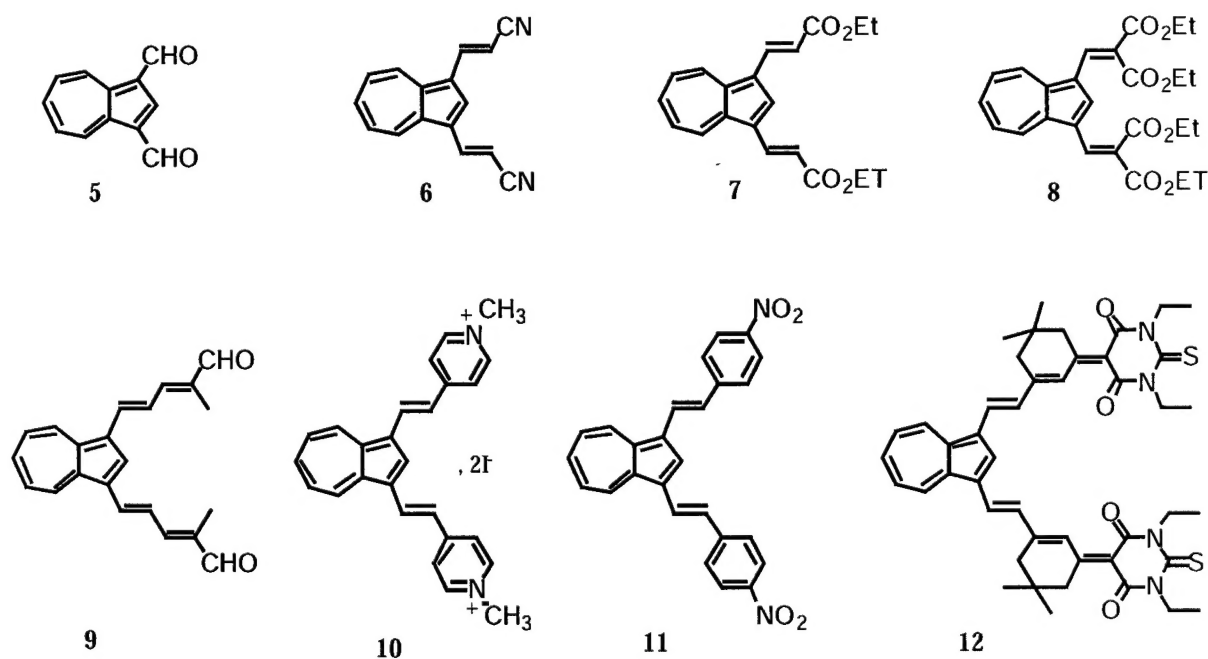
A similar situation might also arise upon electron transfer in azulene-1,3-dicarboxaldehyde.



After electron transfer from the seven-member ring to one of the aldehyde carbonyls the charge-transfer form consists of a new aromatic tropylium carbocation fragment and a resonance-stabilized oxonol anion fragment. To our knowledge this design concept for a NLO chromophore has yet to be tested and might exhibit interesting excited state behavior and optical nonlinearities.

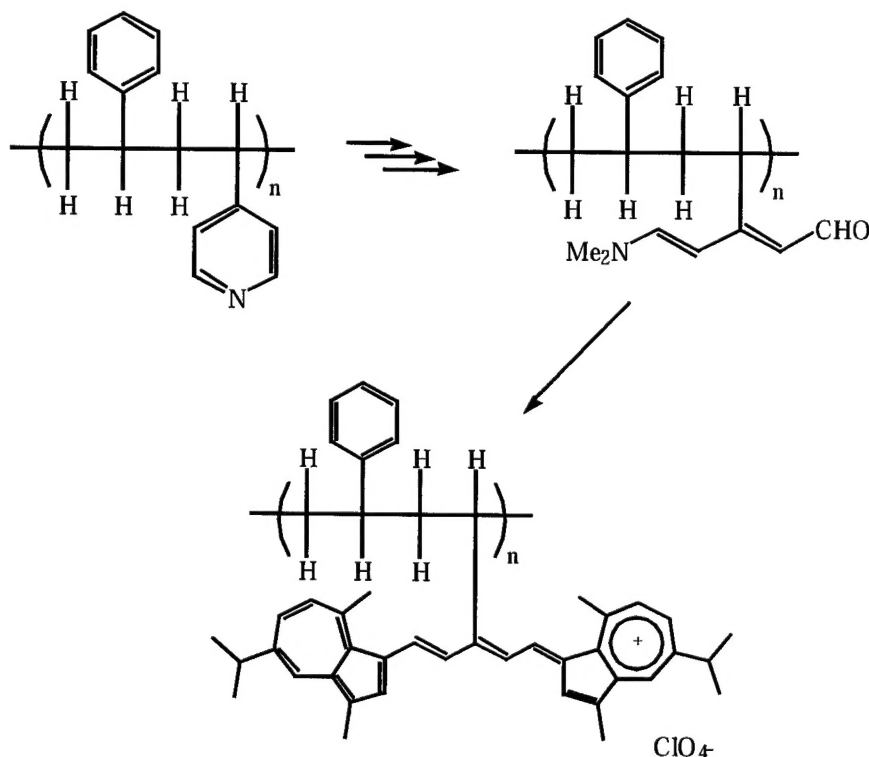
Several new 1,3-disubstituted azulenes have recently been prepared to test this interesting new concept (See list below). Unfortunately, we have not been successful to date in making 1,3-bis-immonium salt, I.

List of symmetrical azulene-containing chromophores



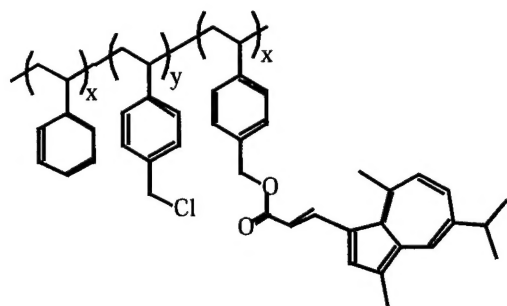
II. Azulenic NLO Polymers

In an earlier project we succeeded in preparing a variety of new azulene-containing NLO polymers for potential second- and third-order NLO applications including optical limiting. In a preliminary study we converted poly(styrene-*co*-4-vinylpyridine) to a pendant merocyanine which we later coupled to guaiazulene to give the desired product, a guaiazulenic pentamethine dye covalently attached to a polymer backbone.

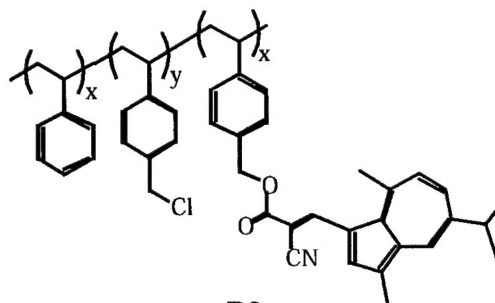


The absorption spectrum for the crude polymer was essentially the same as for the free chromophore with λ_{max} at 901 nm. We have not characterized this important material other than determining the approximate molecular weight of the starting copolymer by gpc (using a borrowed Waters Styragel HR 4E GPC column). Further analysis of our materials awaits approval of a pending DURIP 99 request for a GPC and DSC or establishing a collaboration with NLO polymer researchers to carry out this important work.

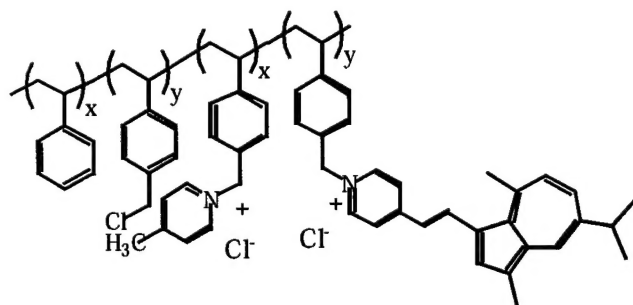
Since that time we have developed a new synthetic methodologies for conveniently attaching the azulenic chromophore to a polymer matrix. New polymers are illustrated below.



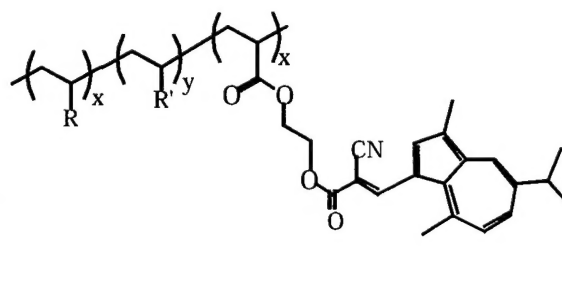
P1
 $\lambda_{\max} = 413 \text{ nm}$



P2
 $\lambda_{\max} = 455 \text{ nm}$

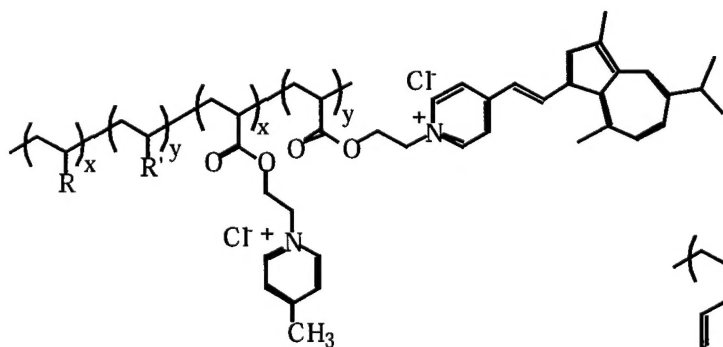


P3
 $\lambda_{\max} = 517 \text{ nm}$

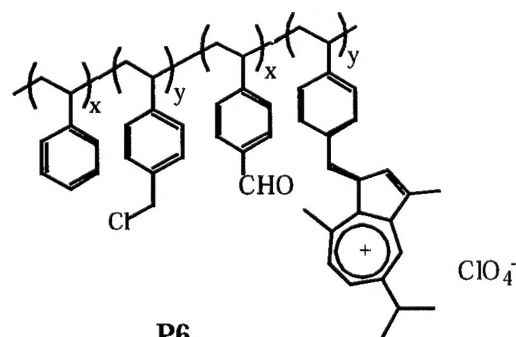


P4
 $\lambda_{\max} = 455 \text{ nm}$

R = CO₂CH₃
 R = CO₂CH₂CH₂Br



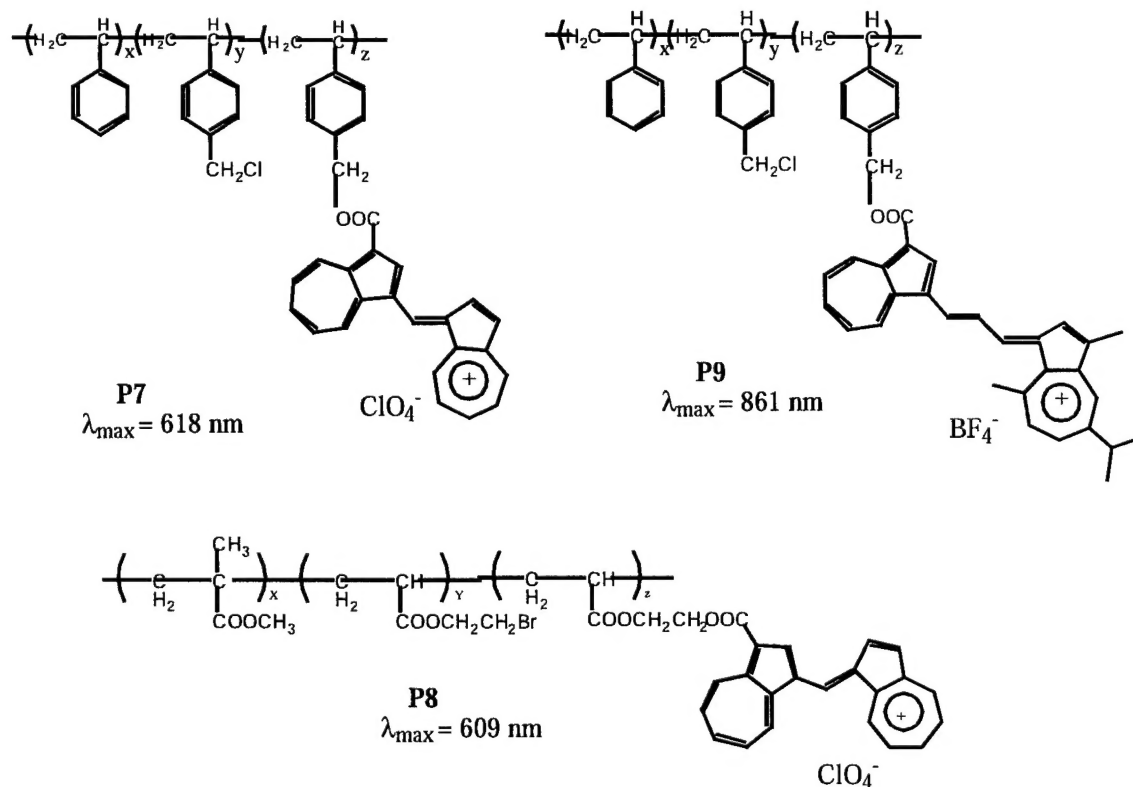
P5
 $\lambda_{\max} = 502 \text{ nm}$
 R = CO₂CH₃
 R = CO₂CH₂CH₂Br



P6
 $\lambda_{\max} = 462 \text{ nm}$

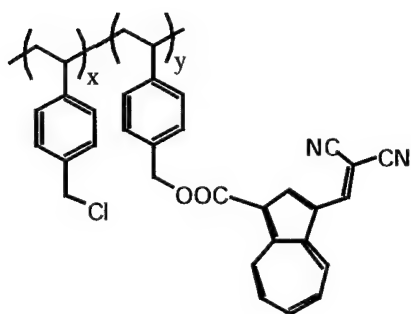
Polymers **P1-P6** were prepared by sequential modification of poly(vinylbenzyl chloride) or poly(methyl acrylate). The guaiazulenyl moiety was attached by straightforward esterification (**P1**, **P2** and **P4**), base-catalyzed condensation (**P3** and **P5**), and acid-catalyzed condensation (**P6**).

Polymers **P7-P9** are azulenic polymethine dyes covalently attached to poly(vinylbenzyl chloride) and poly(2-bromoethyl acrylate) by esterification with azulene-1-carboxylic acid followed by acid induced dye formation using azulene (**P7** and **P8**) or 3-(1-guaiazulenyl)propanal (**P9**).

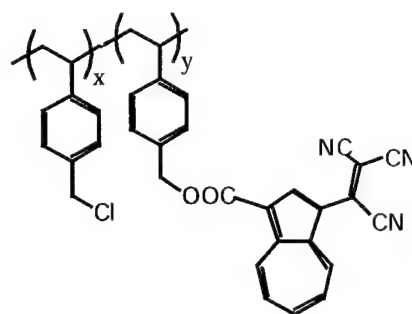


The blue shift in absorption maxima for **P7** and **P8** compare to the free dye **1** (page 1) is partly attributable to the absence of alkyl groups on the chromophore. On the other hand, the λ_{\max} of polymeric dye **P9** is considerably red-shifted relative to model compounds. We have no explanation for this behavior at present.

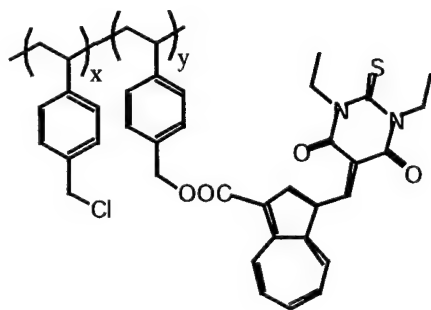
Lastly, polymers **P10 -P12** contain novel unsymmetrical "pull-pull" azulenenes with two different electron-withdrawing groups at C1 and C3 of the azulene ring. The observed blue-shifts in λ_{\max} for these compounds is consistent with both the presence of an electron-withdrawing carboxyl group on the five-membered ring and a hydrophobic environment.



P10
 $\lambda_{\text{max}} = 412 \text{ nm}$



P11
 $\lambda_{\text{max}} = 500 \text{ nm}$



P12
 $\lambda_{\text{max}} = 459 \text{ nm}$

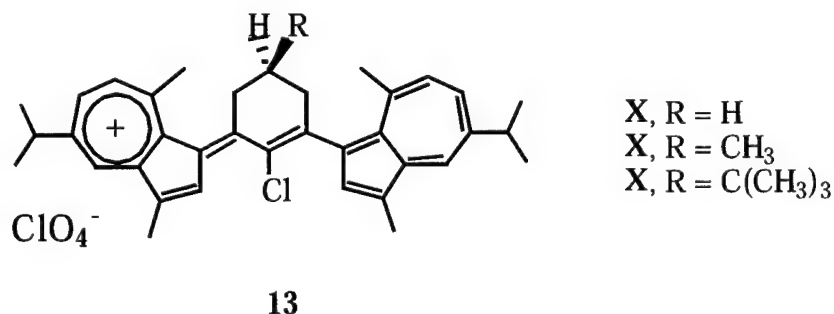
We are continuing our efforts to further refine our synthetic protocols to improve both final polymer homogeneity and loading. Since much of this chemistry is new we are also exploring other research directions for some of the difunctional chromophores.

III. ^1H -NMR Study of a Guaiazulenic Polymethine Dye.

Among the various classes of chemical structures with large third-order optical nonlinearities the highly conjugated symmetrical cyanine and structurally similar polymethine dyes have been previously identified as reverse saturable absorbers and potential candidate materials for optical limiting applications.¹² In collaboration with Natick ARO scientists and other academic researchers we reported on the NLO properties of a novel class of third-order NLO chromophore, the azulenic polymethine dyes. These new chromophores, devoid of

heteroatoms, exhibited large third-order susceptibilities $\chi^{(3)}$ -values ranging from 10^{-8} to 10^{-9} esu, and were also optical limiting.^{1,5}

In order to gain additional insight into the salient structural factors that contribute to large NLO effects and to the enhancement of optical limiting thresholds we recently initiated a study of the electronic properties of our polymethine dyes by ^1H - and ^{13}C - NMR spectroscopy. The dyes exhibit weak positive solvatochromism consistent with a highly delocalized electronic structure. Inspection of the chemical structure of salts such as 13c suggested that the counteranion might be situated closer to the ends of the molecule rather than the middle on steric grounds. In this scenario any change in π -electron distribution might be reflected in changes in chemical shifts or coupling constants of the vinylic and aromatic hydrogens upon varying the dye concentration, solvent polarity, or temperature. Since the polar dyes were only partially soluble in nonpolar solvents we carried out this preliminary study using CDCl_3 , CD_2Cl_2 , and acetone- d_6 . The probe temperature was varied from room temperature to -90°C . Below this lower limit the salts usually began to crystallize out as evident from spectral line broadening. In all solvents the signals for the ring hydrogens were shifted to higher field. The aromatic hydrogen, H_4 , hydrogen adjacent to the isopropyl group on the seven-member ring was shifted by $\delta 0.45$ ppm upon lowering the temperature. However, for the meso-chlorinated, ring-locked polymethine dye 13c in acetone- d_6 an unusual dynamic behavior was observed for the isopropyl doublets. The variable temperature ^1H -NMR spectra for 13c are shown below.



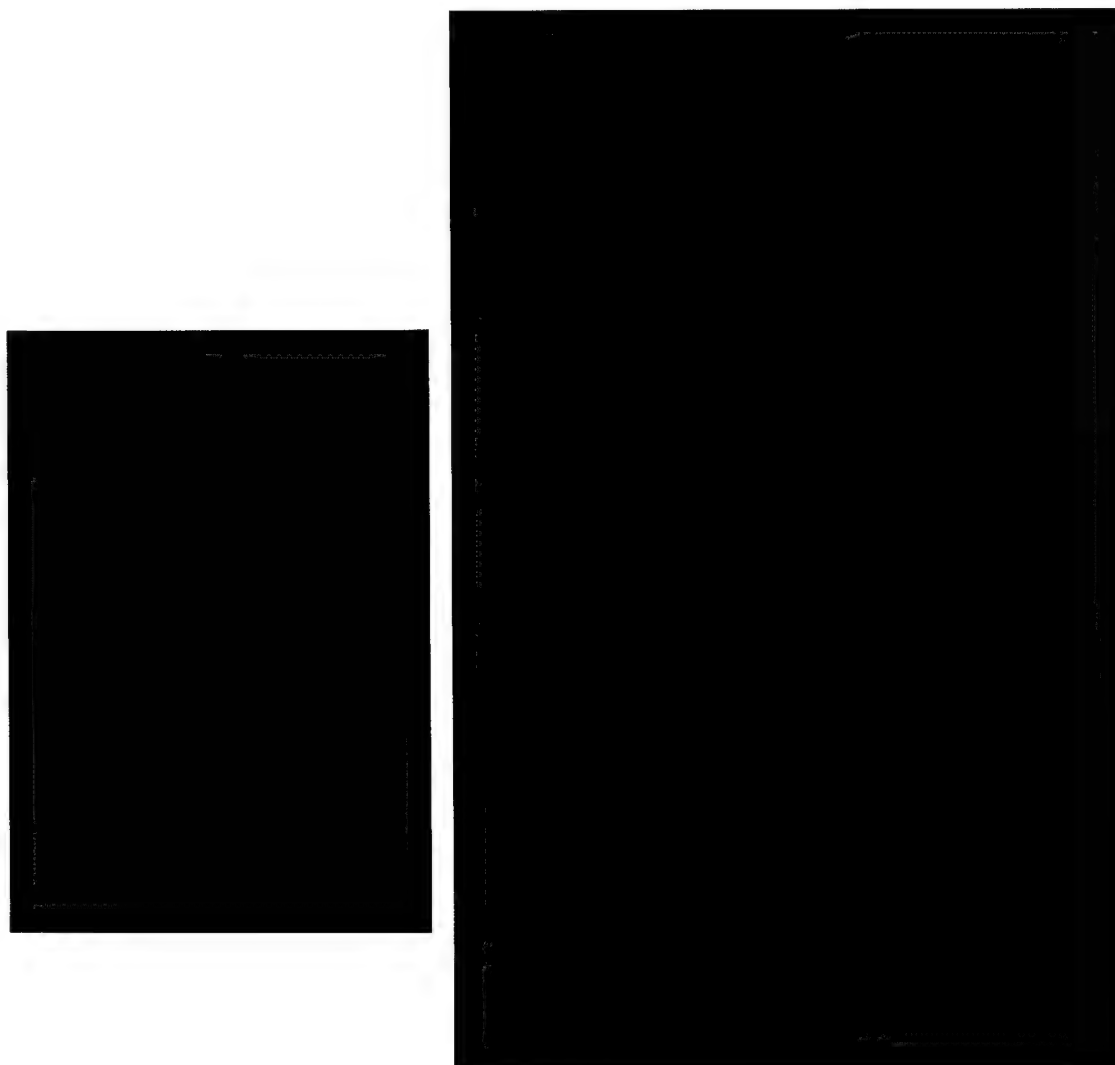


Fig 2. ^1H -NMR spectra of **13c** (400 MHz, acetone- d_6). Upper right: room temperature, CH_3 doublet centered at $\delta 1.43$ ppm; Lower right: -90°C , two CH_3 doublets centered at $\delta 1.34$ and 1.40 ppm; left: splitting of two isopropyl CH_3 signals at -10° , -35° , -50° , and -90°C .

The reason for the temperature dependent splitting of the isopropyl signals was not evident at first. The obvious explanation of nonequivalence of the two halves of the symmetrical molecule due to localization of positive charge on one of the two azulene end groups at low temperature suffers from at least two drawbacks. First, the explanation is equivalent to the claim of freezing out a resonance canonical form, an unlikely situation. Second, if indeed the positive charge is somehow localized on one of the azulenes, then one would expect doubling of all signals for the two halves of the molecule. Upon reflection, we began to suspect that the nonequivalence of the isopropyl group methyl signals is due to diastereotopism induced by the perchlorate anion.

For **13c** the exact nature of the molecular asymmetry is not immediately apparent. The only likely candidate for a new chiral center in the molecule is the six-member ring carbon bearing the t-butyl group. Azulenic chromophores without alkyl substituents on the central ring as well as acyclic azulenic dyes did not exhibit temperature dependent splitting of any signals.

A tentative explanation for the observed results is that at sufficiently low temperature the perchlorate anion is asymmetrically situated with respect to the two halves of the otherwise completely symmetrical chromophore. The effect is definitely associated with the presence of a t-butyl group on the six-membered central ring and, quite possibly, the meso-chloro substituent might also play a role. Either or both of these substituents apparently prevent the anion from adopting a position in the symmetry plane of the molecule. Essentially the same dynamic behavior for **13c** was observed upon changing the counterion from perchlorate to fluoroborate. Replacing the bulky t-butyl with a smaller methyl group **13b** also gave rise to the same temperature dependent splitting as in **13c**. In contrast, no temperature dependence on the chemical shift of the isopropyl methyls was observed for the parent structure **13a** or for acyclic azulenic polymethine dyes. Interestingly, no splitting was observed in chlorocarbon solvents at any temperature studied.

One possible explanation for the observed solvent specific dynamic NMR behavior involves intermolecular association (dimerization, M-aggregation?) that somehow induces a dissymmetric environment. While our explanation for this intriguing NMR result is only tentative, it does raise the possibility of controlling the bulk properties of polymethine dyes by appropriate substitution of the chromophore or by regulating properties (polarity, viscosity, etc.) of the host media. It would be interesting to study the behavior of azulenic polymethine dyes in in a polar polymer matrix.

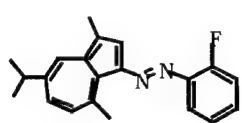
IV. Stark Spectroscopy of Fluorinated Azulenic Azobenzenes

Electroabsorption (Stark) spectroscopy is useful for the direct determination of ground and excited state dipole moments, μ_g and μ_e , respectively, transition dipole moments, $\Delta\mu$, and polarizabilities, α , for NLO donor-acceptor chromophores immobilized in a frozen matrix or polymer host. From these data the static first hyperpolarizability β_0 can be readily determined. Substitution of hydrogen with highly electronegative fluorine in the acceptor portion of donor-acceptor molecules enhances second-order susceptibilities, $\chi^{(2)}$, and significantly reduces

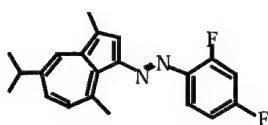
refractive indices of organic materials (a useful property to control for the tuning of optical waveguides, for example).^{13,14} Linear absorption properties are also highly dependent on the position of attachment of fluorine substituents on polyenal (both conventional retinal analogs and azulenic retinal analogs) chromophores when incorporated into the chromoproteins, rhodopsin and bacteriorhodopsin. For a side-chain fluorinated guaiazulenic trienal, the absorption maximum of the corresponding azulenic bacteriorhodopsin analog was dramatically red-shifted into the near-IR ($\lambda_{\text{max}} = 795 \text{ nm}$). Another remarkable change in photophysical properties was reported by this Laboratory in a collaborative study with Dr. Ron Steer of U. Saskatchewan.⁴ Replacement of ring hydrogens with fluorine at the 1- and 3-positions of azulene led to a decrease of the S_0 - S_1 bandgap ($11,880 \text{ cm}^{-1}$) with a highly unusual concomitant increase in the S_0 - S_2 bandgap ($16,100 \text{ cm}^{-1}$). As a consequence its S_2 fluorescence lifetime was increased to *ca.* 10 nsec and fluorescence quantum yield was greatly increased relative to the parent hydrocarbon ($\Phi_F = 0.2$ and 0.04 for 1,3-difluoroazulene and azulene, respectively, with EtOH as solvent). Oxidation-reduction potentials for a wide variety of azulenic compounds were also determined and found to correlated with Hammett σ -constants.¹⁵

In collaboration with Professor Hideki Hashimoto of Shizuoka University, Japan, we are currently investigating the electronic properties of a series of fluorinated azulenic donor-acceptor chromophores by Stark spectroscopy.

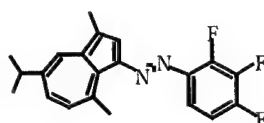
Structures of Fluorinated Guaiazulenenic Azobenzenes



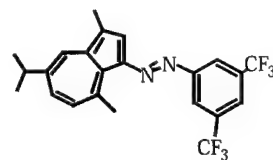
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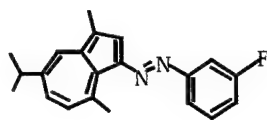
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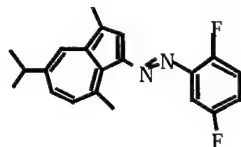
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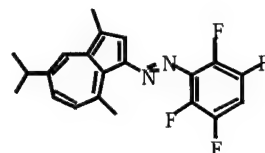
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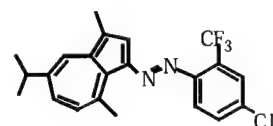
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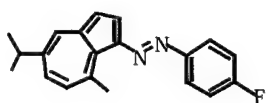
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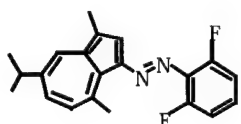
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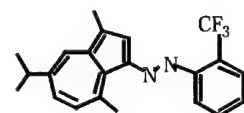
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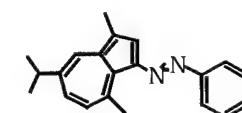
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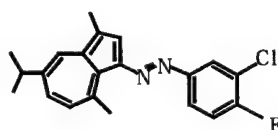
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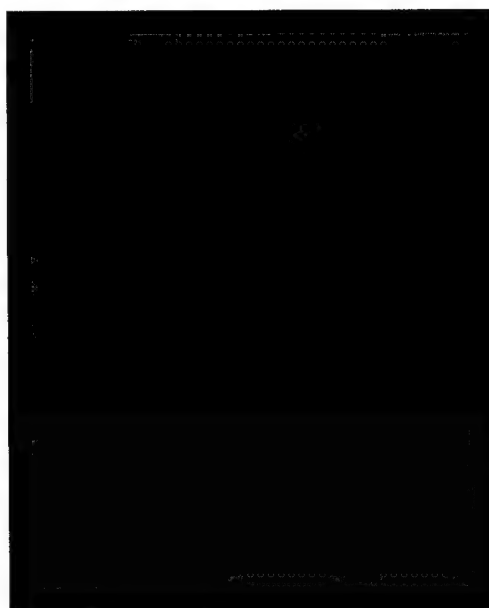
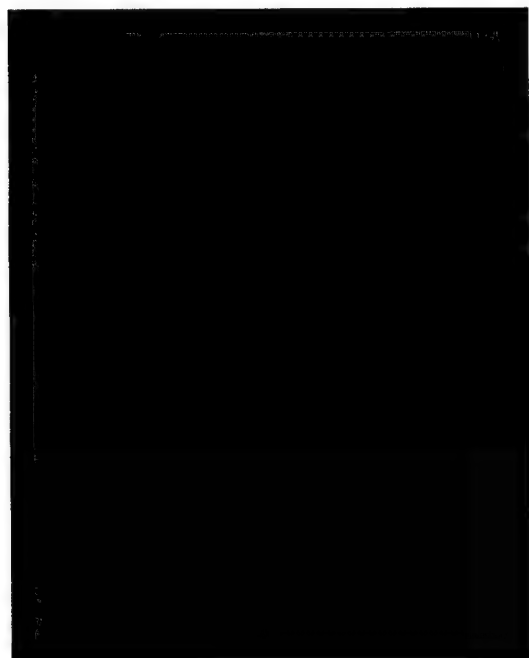


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Initial results for a few of our compounds in a PMMA matrix (5 wt %) are shown below. Fine-structure in the Stark spectrum suggest the presence of multiple transitions. We are presently analyzing the Stark spectra of our fluorinated compounds and calculating spectral transitions by the ZINDO/CI method.



	$\Delta\mu$ (D)	$\beta / 10^{-28}$ esu	$ \gamma 10^{-33}$ esu
DW10	4.6(2)		
DW12	4.5(3)	0.92(6)	0.75(3)
DW13	5.2(2)	1.19(4)	0.88(2)

V. Theoretical Calculations

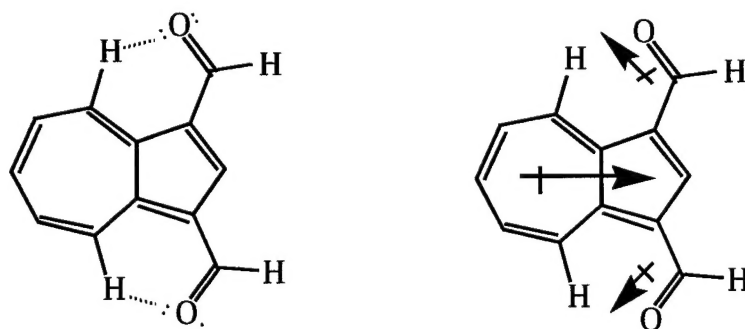
We have already established that azulene is an excellent π -electron donor in NLO chromophores and that azulenetic carbocyanine dyes are reverse saturable absorbers and optical limiters. To augment our ongoing program of preparing new azulenetic chromophores with enhanced optical nonlinearities and optical limiting performance, we have employed the semiempirical AM1/FF and ZINDO/S-CI quantum chemical methods to gain additional insight into critical factors such as molecular orbital energy levels, ground and excited properties, and the role of substituents.

In collaboration with Professor C. Ye of Beijing molecular hyperpolarizabilities, dipole moments, and linear absorption properties were calculated for a number of donor-acceptor substituted azulenes. These results confirmed that azulene was an efficient bridging moiety between donor and acceptor groups in addition to being an excellent π -electron donor in its own right. Interestingly, azulenes with 1-donor and 5-acceptor groups were found to have large β values and small dipole moments which might be useful in reducing intermolecular electrostatic interactions (*i.e.*, aggregation) and increasing order parameters and chromophore loading levels when incorporated into a polymer host.³

We also recently looked at the effect of successive replacement of the 1-, 2- and 3-hydrogens of azulene with fluorine and carboxaldehyde substituents on transition energies between S_0 , S_1 and S_2 as well as other MO properties (orbital coefficients).⁸ Both the position of attachment and the nature of the substituent were found to influence energy levels and band gaps. The S_1 energy level was predicted to drop below S_2 for azulenes substituted in the 1-position with a conjugated side chain (*i.e.*, polyenal). In contrast, S_1 and S_2 were unchanged in 2-substituted azulenetic retinals. Inversion of the A_g and B_u excited states has been reported for retinal and symmetrical cyanines.

Theoretical analysis of potential azulenetic two-photon absorbing chromophores, the symmetrical 1,3-disubstituted azulenes, revealed an interesting conformational preference for azulene-1,3-dicarboxaldehyde, a key compound in this emerging study. In its most stable conformation both carbonyl groups are pointing back toward the seven-membered ring. This orientation, contrary to steric considerations which would predict just the opposite orientation, can be rationalized by favorable dipole-dipole interactions between azulene and carbonyl groups.

Alternatively, there is also the possibility of hydrogen bonding between 4-H and 8-H on the seven-membered ring and the carbonyl oxygens. Hydrogen bonding between C-H and O (C-H \cdots O), is less favorable than hydrogen bonding between O, N, and H, but has been invoked in special circumstances.



Dr. Rajeev Muthyala also calculated theoretical absorption maxima and oscillator strengths for the two principal long wavelength absorption bands of azulene and several of its derivatives by the ZINDO/S-CI approach.¹⁶ His calculations indicated that introducing electron-withdrawing substituents at the 1-position of azulene results in greater contributions by HOMO-1 and LUMO+1 energy levels to the S_1 and S_2 transitions. His results also confirmed the increase in the S_0 - S_1 energy gap with increasing conjugation (blue shift in λ_{max} of S_1).

We have also recently embarked on a collaboration with Professor John Head here at U. Hawaii to calculate excited state properties of various azulenic chromophores in order to explain some intriguing results from earlier experiments. For some time now we have been baffled by the lack of a photocycle in azulene-containing bacteriorhodopsin analogs. Azulenic retinals also fail to undergo photoisomerization when irradiated. And in another surprising observation, the isopropyl methyls on the guaiazulene end group for certain pentamethine dyes exhibit dynamic NMR behavior, ultimately separating into two well-resolved pairs of doublets (See NMR section). One possible scenario for this hitherto unprecedented observation is that at low enough temperature in acetone- d_6 solvent the perchlorate counterion is immobilized in the immediate vicinity of one of the isopropyl groups rendering it magnetically nonequivalent to the other isopropyl. It would be of more than passing interest to examine the temperature effects on linear and nonlinear absorption properties including optical limiting thresholds for the azulenic polymethine dyes and related chromophores.

VI. References

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